SEPARATION OF URANIUM FROM AN AQUEOUS SOLUTION OF URANIUM AND MOLYBDENUM BY FOAM FRACTIONATION

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CERTIFICATE

This is to certify that this work has been carried out under my supervision and has not been submitted elsewhere for a degree.

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Author

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ABSTRACT

The present study was carried out for the separation of uranium from molybdenum from their mixtures in dilute solution, by foam fractionation. In the present investigation, uranium was separated from molybdenum by foaming the solution containing benzethonium chloride as surface active agent. Continuous counter current studies were made. A fractional factorial design of experiments was used to organize the experiments. Variables used for study were concentration of uranium, concentration of molybdenum, concentration of benzethonium chloride, normality of hydrochloric acid, reflux rate, feed point location, gas flow rate. Following values are recommended.

Concentration of uranium	= 1 mg/100 ml
Concentration of molybdenum	= 1 mg/100 ml
Concentration of benzethonium chloride	= 250 mg / 100 ml
Normality of hydrochloric acid	= 8
Reflux Rate	= 2 ml/min.
Feed point location	= Datum level
Gas Flow Rate	= 15 ml/min.

CHAPTER 1

INTRODUCTION

In general, separation techniques are based on differences in physical properties, for example, distillation is based on the difference in volatility of the components to be separated, The extraction operation works because of the difference in solubility of the solute. Separation by foam fractionation is possible because of the difference in the surface activity of the constituent solutes. Thus surface active compounds can be separated from their solutions because of the differences in their surface activity. If one is desirous of removing a surface-inactive compound from a solution, one can add a surface active compound of opposite charge.

1. to combine with it electrostatically to form a surface active compound.
2. or form a chelate or a complex with the surface-inactive material which will then be rendered surface active and separated by foaming.

Foam-fractionation is a technique for partially separating or concentrating dissolved materials by adsorption at the surfaces of bubbles, which riseup through the liquid poor, forming a foam to be collected and broken up to recover the solute. Since no heat input is required in foam-fractionation, it can be used to separate chemically unstable, heat sensitive materials which cannot be easily separated by conventional separation

techniques. This works best in very dilute solutions and is very effective for separation and purification of costly materials present in traces. It can also be used for the removal of small amounts of colloidal or suspended material from large volumes of liquid. There may be new applications in the separation of chemically similar substances, based on inherent or induced differences in their surface-activity.

Generally speaking, a surface-active molecule is hydrophobic at the polar end and hydrophilic at the non polar end, which renders one end of the molecule relatively soluble in a solvent and the other end relatively insoluble. Thus the molecule as a whole is 'happiest' at the gas-liquid interface with the soluble end in the solvent and the insoluble end sticking out into the gas phase. In an effort to approach this state, many of the molecules migrate to the interfacial surface of the bubbles rising through the liquid pool and are thus carried up into the foam. Foam fractionation differs from flotation as the later deals with heterogeneous systems while former with a homogeneous systems.

In the present study, uranium was separated from a mixture of uranium and Molybdenum in HCl medium by foam-fractionation. Uranium gives anions in HCl medium while Molybdenum does not. The extraction of uranium is dependent upon ion-association of surfactant ion with the uranyl chloroanonic complex. The resulting surface active compound then can be foamed by

bubbling N_2 gas, and separated from Molybdenum. One of the objectives of the present study is to try several surfactants and isolate the surfactant that has most efficient foam characteristics. It is proposed to establish the feasibility of operation. The following are the variables for study:

1. Initial concentration of uranium
2. Initial concentration of Molybdenum
3. Concentration of surface-active agent
4. Normality of hydrochloric acid
5. Reflux ratio
6. Feed point location
7. Gas flow rate.

In view of the large number of variables mentioned above, it would be necessary to make a fractional factorial design of experiments in order to get maximum information with minimum number of experiments.

The chosen system has a good deal of scope in the Indian context. In the process plant of Uranium Corporation of India, waste streams containing Uranium and Molybdenum in dilute quantities do occur. If the present study establishes the feasibility of Uranium recovery from dilute solutions then it can be very well utilized for the separation and recovery of Uranium & Molybdenum from such waste streams. Molybenum also happens to be an important metal that is required for special alloys used in defence and other vital industries. Feasibility

of foaming of Uranium could also lead perhaps to enrichment of Uranium. At any rate the technique could be used and has been shown to be useful by earlier research workers for separation of constituents from irradiated fuel elements. The present investigation is only a technical feasibility study and by no means an exhaustive study because of the limitations of time. It is also not a techno-economic feasibility study.

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CHAPTER 2

LITERATURE REVIEW

There has been a growing interest in recent years in the separation of materials by foam fractionation and related techniques. Procedures, once just laboratory curiosities, are now feasible for the purposes ranging from chemical analysis to plant scale operation.

One of the earliest study on foam fractionation was removal of oleate from aqueous solutions in an attempt to verify experimentally the Gibb's adsorption equation.[1] Concentration of metal ions by foam fractionation was carried out for the first time by Sebba[2] Rubin in an excellent review listed 18 metals, 14 dyes, 4 organic anions, 21 fatty acids and detergents, 22 proteins and enzymes, and some miscellaneous inorganic ions and organic substances which could be separated by foam fractionation[3].

The separation from water of anionic surfactant aresket 300[4], the cationic surfactant ethyl hexadecyldimethyl ammonium bromide[5,6] at various temperatures[7] in the presence of inorganic acids and bases[8] and other surfactants [9,10] were thoroughly investigated. Sodium phenolate from waste water was removed by surfactant cetyltrimethyl ammonium bromide[11].

Methyl orange and protonated 1-napthyl-amine were successfully removed by foam fractionation utilizing the oppositely

charged surfactant sodium lauryl sulfate[12,13]. Under nearly total reflux condition, the recovery of methyl orange was essentially complete[14]. Selective separations of one ion from another have been reported. Aluminium has been separated from Berillium at a pH 4.

Some of the recent publications in the area, particularly since 1969 have been reviewed below. Foam separation of solutions containing two ionic surface active solutes, sodium lauryl sulfate and sodium dodecyl benzesulfonate, was carried by Rubin[15] in 1969. According to him the determination of surface excess for solutions containing a single surface active solute from the surface tension concentration data does not necessarily predict the results obtainable by foam separation. But the surface tension data may serve as a good indicator for determining the critical micelle concentration of solute. Hargis[16] also in 1969 evaluated the possible role of the competition for the interface in foam fractionation by studying the enrichment of sodium dodecyl sulfate, sodium benzesulfonate and sodium dodecyl benzesulfonate, by foaming alone and in binary mixtures. A decrease in the enrichment ratio owing to the presence of the second surface active compound was not observed. Since the enrichment ratio for a surface active substance is higher at lower concentrations, the attempted separation from a solution of large concentration of a more surface active substance and a small concentration of a less active substance can result in nearly complete removal of the

latter in the foam.

Bikerman[17] used eleven foaming agents to determine their effectiveness in removing Fe^{2+} and Mn^{2+} ions from aqueous solutions by the foam fractionation technique. Among the surfactants used, the anionic detergents yielded a better fractionation than nonionic materials. Kondratacıums[18] was successful in removing synthetic surface active agents from waste water of tanneries[19] The separation of species present in traces in solutions have been studied by Karger[20]. He studied the removal of anionic chloro-complexes of Fe^{3+}, Hg^{2+}, and CO^{2+}, using hexadecyltrimethyl ammonium bromide surfactant.

Rubin[21] found that ionic charge and size of the species present govern the selectivity of surface adsorption of counterions in foam fractionation process.

Bikerman[22] found that long chain alkyl sulfates and polyoxyethylene sulfates are efficient foaming agents for the partial removal of calcium, iron, and magnese from their salt solutions by foam fractionation. Non ionic surfactants are unsatisfactory in this regard.

An empirical model proposed by Grieves[23] gives the relation of the batch foam fractionation rate as a power function of the air rate and the instantaneous residual surfactant concentration, eliminating the bubble size which is difficult to control and measure for the batch foam fractionation. For the cationic surfactant, ethyl hexadodecylammonium bromide, the

batch foam fractionation rate is directly proportional to the residual surfactant concentration at higher concentrations of the solution. Constants obtained from batch experiments can be used in the corresponding equation for continuous operation, to predict accurately the continuous foam-fractionation rate for a single value of the flow rate of air, and over a substantial range of solution feed-rates, and surfactant concentrations.

Khrustalev[24] developed the kinetic model for the extraction of non ionic surfactants from aqueous solutions. He derived equations for determining the rate and percentage of extraction. A study was made on the rupture of liquid films by New[25] who proposed that a rapid coalescence occurs during the first few minutes. Theory of foam drainage and overflow was developed by Leonard[26]. He considered the interstitial liquid in the continuum phase, in his hypothesis.

Uranium has been separated from vanadium in carbonate medium[27] by Jacobelli. He also separated uranium from thorium in hydrochloric acid medium by means of ion association between the cationic surfactant and uranyl chloroanionic complex[28]. Rabrenovic[29] concentrated uranium from dilute solutions of uranium obtained by leaching low grade uranium ores with sulfuric acid. Fodnek[30] succeeded in extracting molybdenum and tungsten from waste waters at a pH 4.0 using alkyl amines as surfactant. Tiwari and Gopala Rao have reported the removal of nickel from a dilute solution of nickel and cobalt using aerosol-22 which was found to be the best surfactant for the system after extensive studies[31].

CHAPTER 3

EXPERIMENTAL

Chemicals Used

The chemicals used in the investigation were of analar grade uranyl nitrate, molbdenum, and hydrochloric acid. Surface active agents used were. benzethonium chloride, alkyltrimethyl ammonium chloride, benzalkonium chloride, alkenyl dimethyl ethyl ammonium bromide (all these made by Sigma Chemicals Co. of U.S.A.), aerosol-OT, aerosol-18, and aerosol-22 (all these made by American Cyanamide Co. of U.S.A.).

Equipments Used

Equipments used for analysis and experimentation include: centrifuge, a Beckman pH meter, a spectronic-20 spectrophotometry (made by Bausch & Lomb of U.S.A.), surface tensiometer, voltage regulators, electric motors for breaking the foam and mixing the solutions, solution metering pumps for pumping the known amounts of solution. A metler balance for weighing purposes and a gas flowmeter (for calibrating the gas flow) were used.

Apparatus:

A photographic view of the experimental set-up is presented in Fig.(3.1). A schematic diagram is also shown in Fig.(3.2). The foam column A is a corning glass tube, 30 cm. high and 6 cm in diameter and was fitted with a sintered disc which serves as a distributor. On the top of each column,

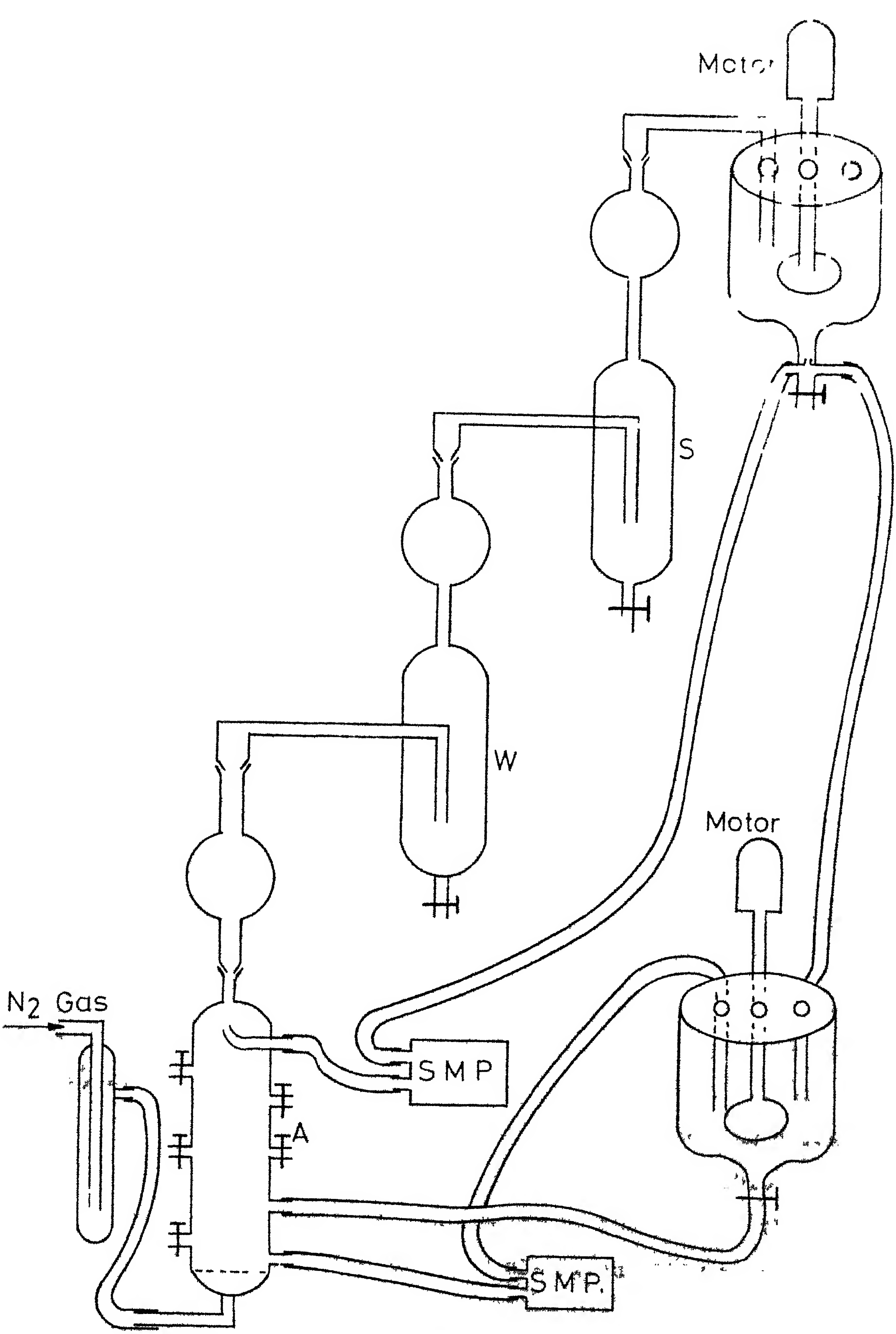


FIG 3 2 SCHEMATIC VIEW OF APPARATUS

there is a globe which serves as foam reservoir. There are four feed points in the foam column along the height. The washing column W, 20 cm. high and 4 cm. in diameter, is connected to the top of the globe by means of a glass joint. As shown in the Fig. (3.2) the washing column inturn is joined to the stripping column S of the same size through another glass joint.

A perforated-basket type mechanical foam breaker 'B' of 6 cm. diameter was used. The perspex blades attached to the outer periphery of the perspex basket give the breaking action to the over-flowing foam. A part of the product stream was recycled back (as reflux) to the foam column by a solution metering pump of 0-5 ml/min. capacity. Rest of the product stream was continuously pumped by a solution metering pump of 0-20 ml/min. capacity, into a mixer 'C'. This mixture constituted the feed for the foam column and was fed to the column by gravity flow.

Experimental Procedure.

A 100 ml of solution containing known amounts of uranyl nitrate, molybdenum powder, and a surfactant in hydrochloric acid was placed in the foam column. Saturated nitrogen gas, at desired flow rate (measured by the pressure drop across a capillary flow-meter) was passed through the bottom of the column to produce foam. The foam is carried up and bubbled into a washing column containing 60 mg of the surfactant and 20 ml of hydrochloric acid to wash away molybdenum from the foam, and then to the stripping column containing 20 ml of distilled water where

uranium is stripped out of the foam into distilled water. The foam was then mechanically broken in the foam breaker, part of it was refluxed back to the foam column and the rest mixed with the raffinate solution in the mixer. As it trickled down the column, the liquid was stripped of its uranium content by adsorption on the foam surface and was withdrawn from the bottom of the column. Product samples from the stripping, washing, and foam column, at different time intervals were colorimetrically analyzed for their uranium content. It was found that the system reached the equilibrium after 5 hours of operation. In actual practice the author run the experiment for 6 hours to be certain about the steady state condition. Product and raffinate streams were analyzed to determine enrichment ratio (E) of uranium. Data from a typical experimental run is presented in the Appendix B and a sample calculation is also shown.

CHAPTER 4

RESULTS AND DISCUSSION

Choice of Surfactant·

A total number of seven surfactants were tried as surface-active agents in the present study. Surface tension versus concentration data, for the four surfactants, are given in Table 4.1, and are plotted in Fig. 4.1. It can be seen that initially at the low surfactant concentration, surface tension decreases with the increase in the surfactant concentration and then exhibits a relatively abrupt change of slope in a narrow range of concentration. This range of concentration is called the critical micelle concentration (CMC). For practical purposes an average of this narrow range of concentration is taken as the CMC value. The CMC values for the other three surfactants are taken from another study[31]. The characteristics of all the seven surfactants are shown in Table 4.2. Enrichment of uranium is the ratio of concentration in the foamate and the raffinate. The results indicate that benzethonium chloride is the best surfactant among the seven surfactants used. Its enrichment is the highest. Since surface activity of a surfactant is maximum at its CMC value, further experimentations were carried out at the CMC value of benzethonium chloride which is 260 mg per 100 ml of solution.

TABLE 4.1

CONCENTRATION VERSUS SURFACE TENSION

Benzethonium Chloride Concentration g moles/lit.	Benzethonium Chloride Surface tension dynes/cm	Benzalkonium Chloride Concentration g moles/lit.	Benzalkonium Chloride Surface tension dynes/cm	Alkyltrimethyl ammonium chloride concentration g.moles/lit.	Alkyltrimethyl ammonium chloride surface tension dynes/cm	Alkenyl dimethyl ethyl Ammonium bromide concentration gmoles/lit.	Alkenyl dimethyl ethyl Ammonium bromide Surface tension dynes/cm.
$2.5x10^{-3}$	60.5	$3.0x10^{-3}$	62.0	$3.0x10^{-3}$	65.0	3.5×10^{-3}	68.0
$3.3x10^{-3}$	56.0	$4.0x10^{-3}$	57.5	$4.0x10^{-3}$	62.0	$5.0x10^{-3}$	62.0
$3.9x10^{-3}$	53.08	$5.4x10^{-3}$	51.0	$5.7x10^{-3}$	54.0	$6.7x10^{-3}$	55.5
$4.8x10^{-3}$	48.0	$6.4x10^{-3}$	45.0	$7.0x10^{-3}$	48.5	$8.0x10^{-3}$	51.0
$5.5x10^{-3}$	44.5	$7.0x10^{-3}$	42.0	$7.6x10^{-3}$	45.0	$9.3x10^{-3}$	46.5
$6.6x10^{-3}$	39.0	$8.0x10^{-3}$	40.0	$9.0x10^{-3}$	44.0	$2.0x10^{-2}$	45.0
$7.5x10^{-3}$	35.0	$9.0x10^{-3}$	38.5	$2.0x10^{-2}$	42.0	$4.0x10^{-2}$	43.5
$8.5x10^{-3}$	32.5	$2.0x10^{-2}$	36.0	$4.0x10^{-2}$	41.5	-	-
$1.0x10^{-2}$	32.5	$4.0x10^{-2}$	34.5	-	-	-	-
$2.5x10^{-2}$	32.0	-	-	-	-	-	-
$3.8x10^{-2}$	31.5	-	-	-	-	-	-

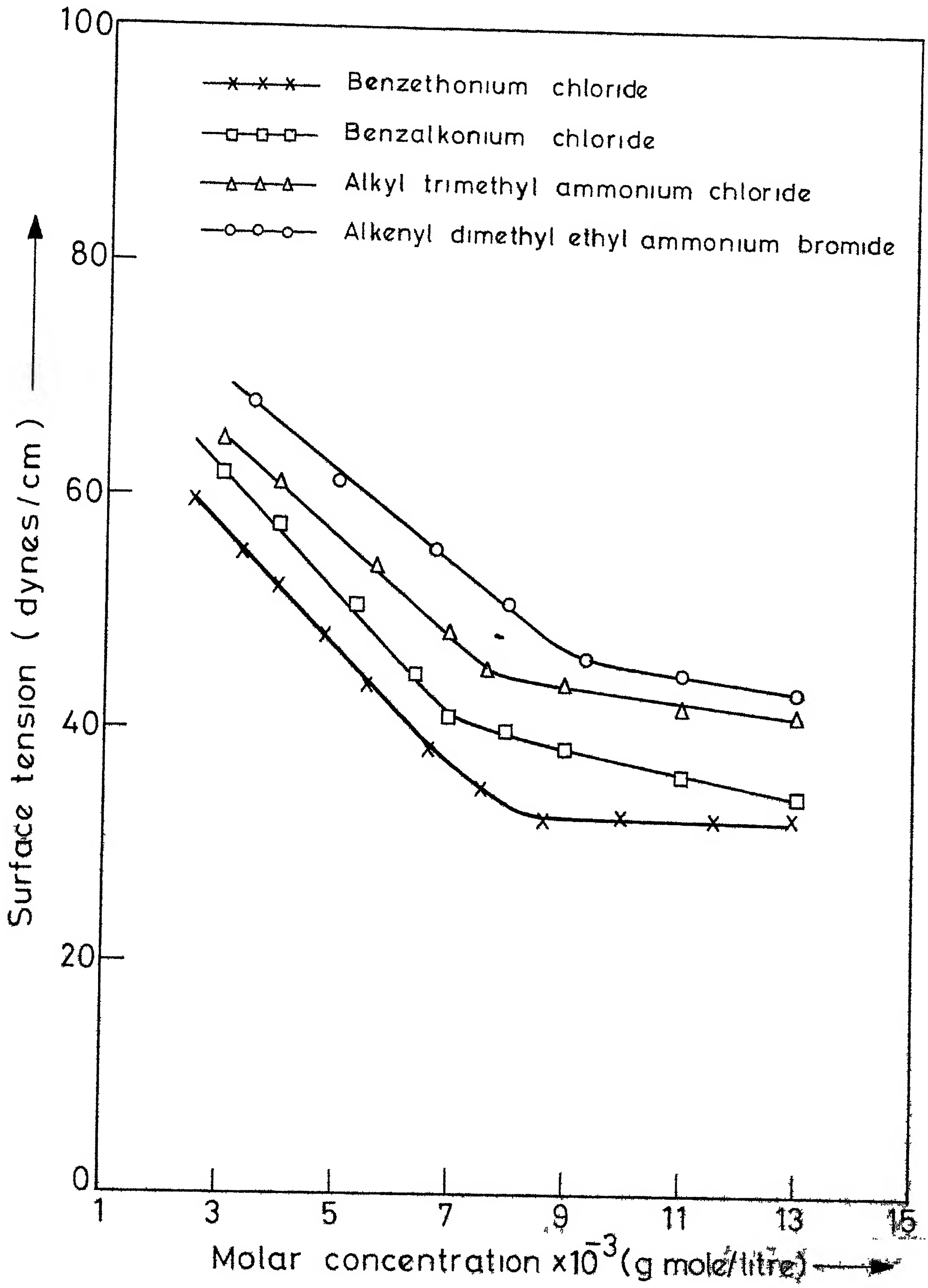


FIG 4.1 SURFACE TENSION VS CONCENTRATION PLOT

TABLE 4.2

RELATIVE SURFACTANT CHARACTERISTICS

Concentration of Uranium = 3.0 mg/100 ml

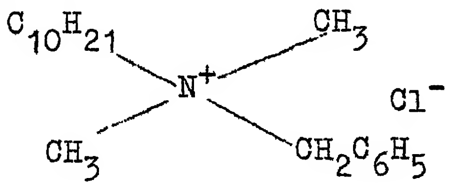
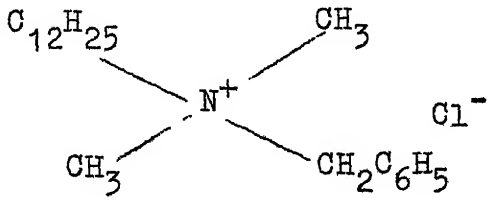
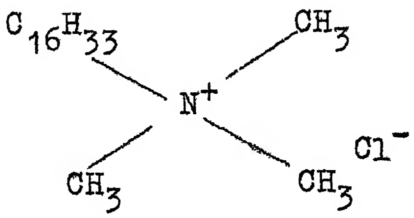
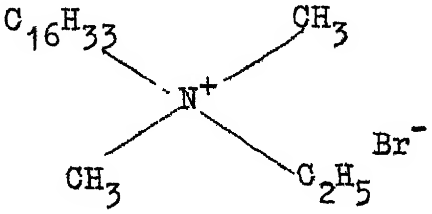
Concentration of molybdenum = 1.7 mg/100 ml

Normality of hydrochloric acid = 6.0N

Reflux Rate = 0 ml/min.

Feed Point = 0 cm.

Gas Flow Rate = 20 ml/min.

Sl. No.	Surfactant	Chemical Structure	CMC	E
1.	Benzethonium Chloride		2.5g/lit.	8.30
2.	Benzalkonium Chloride		2.05g/lit.	2.15
3.	Alkyltrimethyl ammonium chloride(Arquad 16)		6 8g/lit	1.70
4.	Alkenyldimethyl ethyl ammonium bromide(Onyxide)		7.17g/lit.	0.52

5	Aerosol-22	CH_2COONa $CHCOONa$ $CH_2CON<$ $C_{18}H_{37}$ $CHCOONa$ SO_3Na	2,3g/lit	1.75
6.	Aerosol-OT	$CH_2COO\ C_8H_{17}$ $CH\ COO\ C_8\ H_{17}$ $SO_3\ Na$	0.7g/lit	0.43
7.	Aerosol-18	$CH_2CO\ NH\ C_{18}H_{37}$ $CHCOONa$ SO_3Na	0.5g/lit.	2.19

<u>Effect of Normality of Hydrochloric Acid</u>:

As pointed out earlier, uranium gives anions with hydrochloric acid while molybdenum does not. These uranylchloro anions combine with cationic surfactant to give a surface active complex which can then be carried up. Data showing the effect of normality of hydrochloric acid on enrichment of uranium are tabulated in Table 4.3 and plotted in Fig. 4.2. Gas flow rate is a parameter for this study. As is shown in Fig. 4.2, the enrichment of uranium increases with an increase in the normality of hydrochloric acid and is maximum at an 8N solution of hydrochloric acid. But, if the concentration of hydrochloric acid is further increased, enrichment of uranium decreases. The chemistry of uranium compound is quite complicated. An optimum value of 8N solution of hydrochloric acid which is independent of gas flow rate, indicates a particular surface-active anion complex is most stable at 8N hydrochloric acid solution. The identification of this particular anion complex could not be accomplished in this investigation. Enrichment of uranium was found to increase with decrease in gas velocity. This can be explained because of higher residence time and more internal reflux by the collapse of the foam obtained at lower gas velocity At gas velocity lower than 15 ml per minute foam was found to be collapsed and not be carried over. In view of that further experiments were carried out at gas velocity of 15 ml per minute.

TABLE 4.3

EFFECT OF NORMALITY OF HYDROCHLORIC ACID

Concentration of Uranium	3.0 mg.
Concentration of Molybdenum	1.75 mg.
Concentration of Benzethonium chloride	260 mg.
Reflux Rate	0.0 ml/min.
Feed Point	0.0 cm.

Gas Flow Rate = 30 ml/min		Gas Flow Rate = 25 ml/min.	
Normality of Hydrochloric acid	Enrichment ratio of Uranium	Normality of Hydrochloric acid	Enrichment ratio of Uranium
1 0	0.46	1.0	1.00
2.0	0.84	2.0	1.035
3.0	1.00	3.0	1.346
4.0	1.346	4.0	1.83
5.0	2.238	5.0	2.32
6.0	3 263	6.0	5.214
7.0	7.65	7.0	11.00
8.0	8.24	8.0	50.00
9.0	4.57	9.0	10.68
10.0	1.00	10.0	2.24
		11.0	0.46

Table 4.3 (continued)

Gas Flow Rate = 20 ml/min.		Gas Flow Rate = 15 ml/min.	
Normality of Hydrochloric acid	Enrichment of Uranium	Normality of Hydrochloric acid	Enrichment of Uranium
1.0	1.83	1.0	2.238
2.0	1.836	2.0	2.483
3.0	1.95	3.0	2.238
4.0	2.37	4.0	4.16
5.0	4.4	5.0	7.78
6.0	8.33	6.0	17.5
7.0	51.00	7.0	80.67
8.0	80.67	8.0	102.0
9.0	51.25	9.0	90.0
10.0	7.86	10.0	45.0
11.0	1 00	11.0	4.91

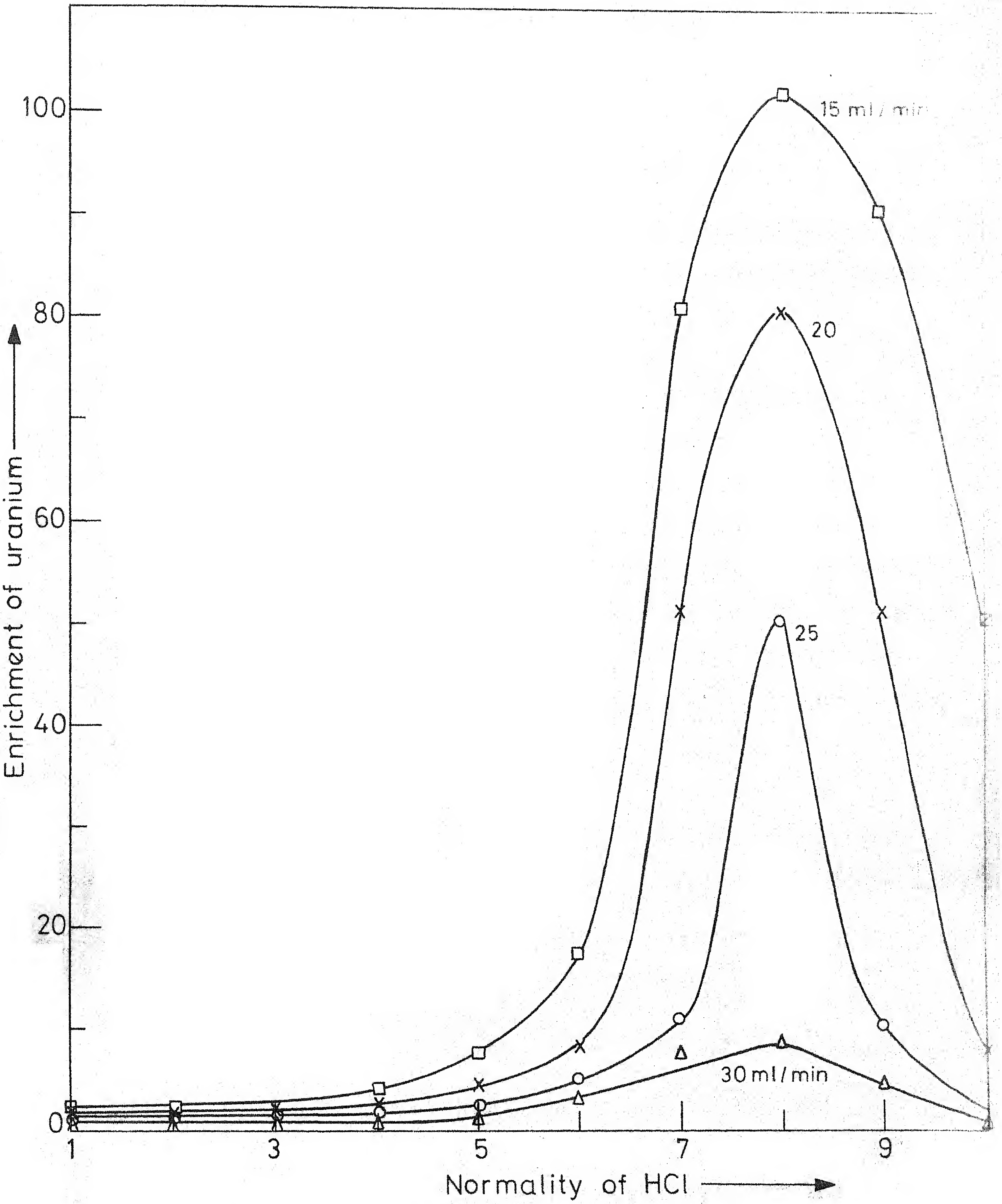


FIG.4.2. NORMALITY OF URANIUM Vs. ENRICHMENT OF URANIUM.

Effect of Surfactant Concentration:

Data in Table 4.4 **show** the effect of concentration of benzethonium chloride on the enrichment of uranium, and the data are plotted in Fig. 4.3. The experiments for finding the effect of concentration of benzethonium chloride were carried out, as explained earlier, at 8.0N hydrochloric acid solution, and at a gas flow rate of 15 ml per minute. Fig. 4.3 indicates that enrichment of uranium is increasing upto a concentration of 250 mg of benzethonium chloride per 100 ml of solution. Further increase in its concentration, decreases the yield of uranium. It is to be recalled that the CMC of benzethonium chloride is 260 mg per 100 ml. and the maximum enrichment is then just below the CMC value of the surfactant. This supports the work of earlier research workers.

Effect of Gas Flow Rate:

Fig. 4.4 shows the effect of gas flow rate on the enrichment of uranium. Data for the plot were obtained from Table 4.3. The plot shows that enrichment of uranium decreases with an increase in the gas flow rate. As mentioned earlier optimum value obtained is 15 ml per minute Further decrease in gas flow rate exhibits a collapse of the foam.

Effect of Concentration of Uranium

Data for the effect of concentration of uranium are given in Table 4.5 and shown in Fig. 4.5. This figure shows that

TABLE 4.4

EFFECT OF CONCENTRATION OF BENZETHONIUM CHLORIDE

Weight of Uranium	3.0 mg.
Weight of Molybdenum	1.75 mg
Normality of Hydrochloric acid	8.0
Reflux Rate	0.0 ml/min
Feed Point	0.0 cm.
Gas Flow Rate	15 ml/min.

Weight of Benzethonium Chloride (mg)	Enrichment Ratio of Uranium
100.0	59.4
150.0	80.0
200.0	93.3
250.0	103.7
300.0	100.0
350.0	90.0
400.0	65.7
450.0	48.8
500.0	37.0

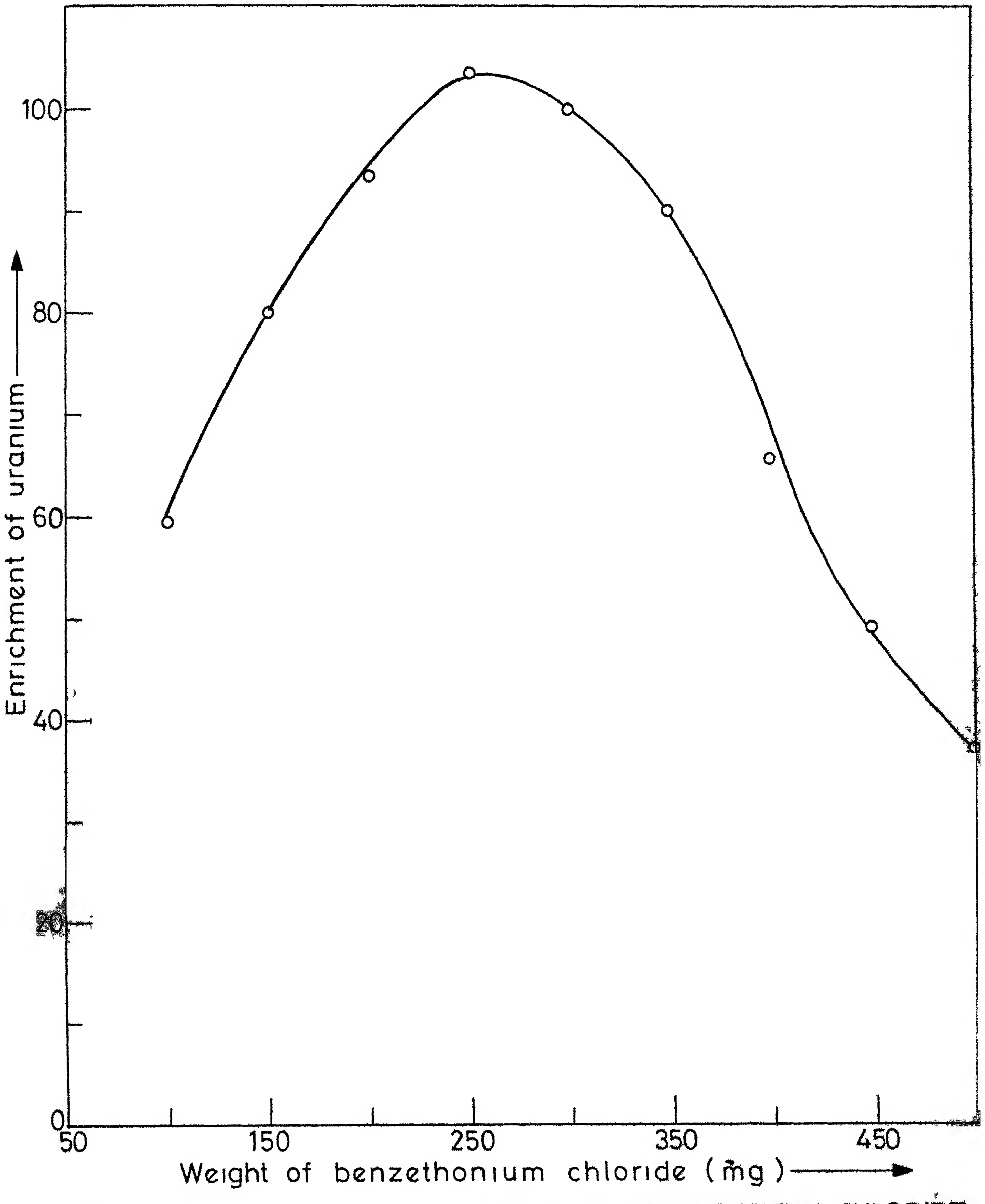


FIG 4.3 EFFECT OF CONCENTRATION OF BENZETHONIUM CHLORIDE

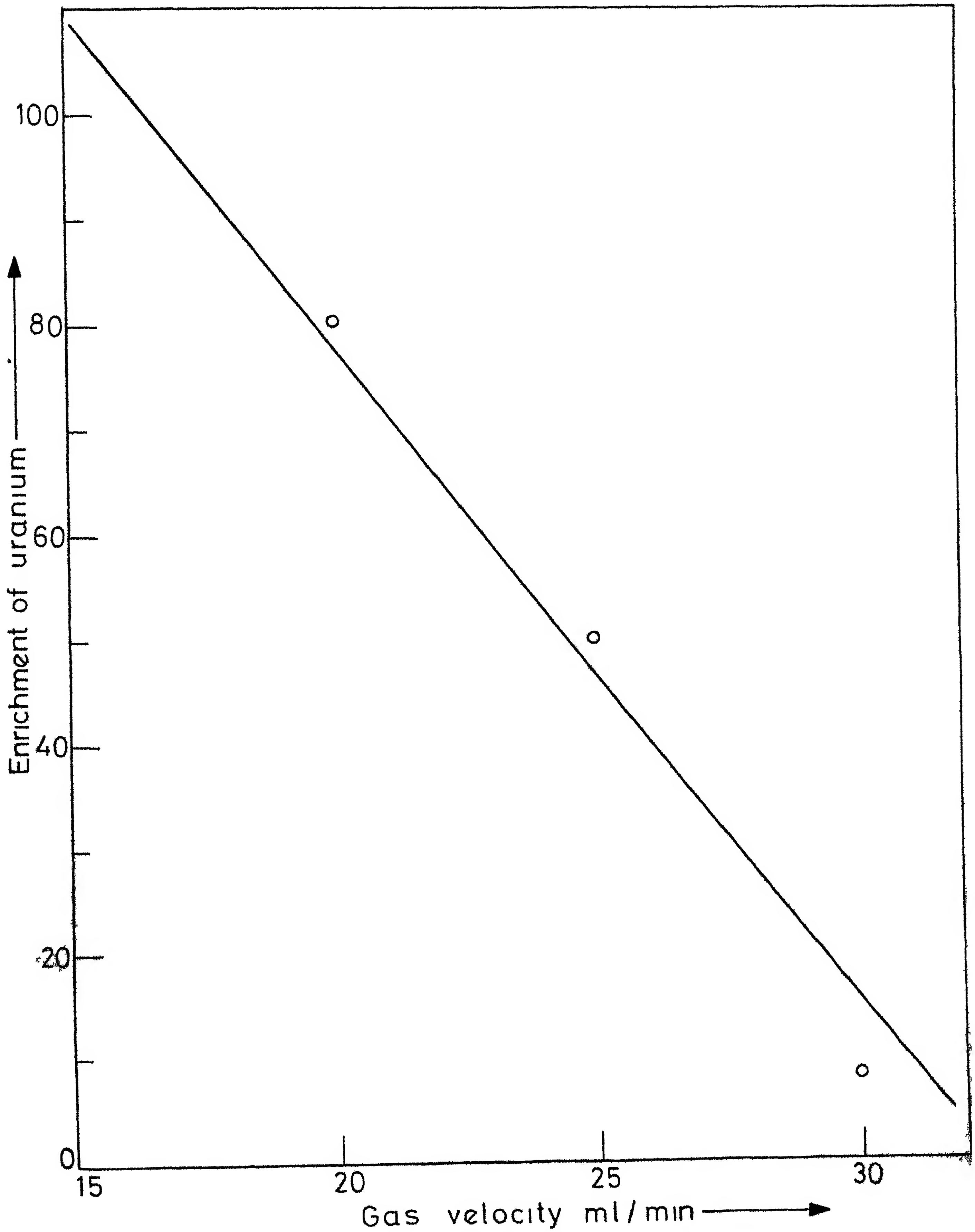


FIG 4 4 EFFECT OF GAS FLOWRATE

TABLE 4.5

EFFECT OF CONCENTRATION OF URANIUM

Weight of molybdenum	= 1.75 mg
Weight of benzethonium chloride	= 250 mg
Normality of hydrochloric acid	= 8
Reflux Rate	= 0.0 ml/min
Feed Point	= 0.0 cm.
Gas Flow Rate	= 15 ml/min.

Sl. No.	Weight of Uranium (Mg)	Enrichment of Uranium
1.	1.0	106.27
2.	2.0	95.53
3.	3.0	93.70
4.	4.0	87 00
5.	5.0	80.00
6.	6.0	40.00

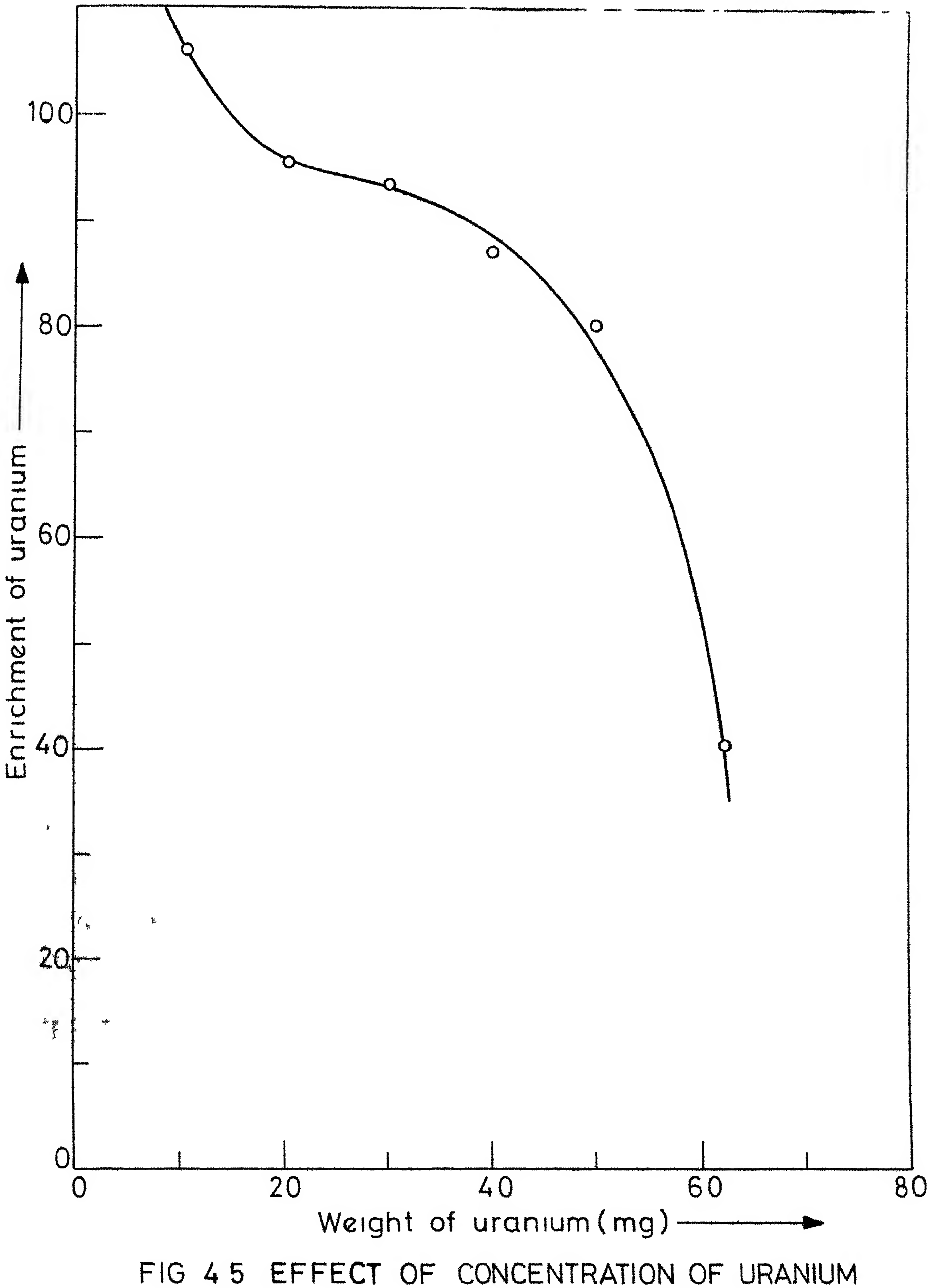


FIG 4 5 EFFECT OF CONCENTRATION OF URANIUM

enrichment of uranium increases with a decrease in its concentration. This confirms the earlier contest that the foam fractionation works the best in very dilute solutions.

Fractional Factorial Design of Experiments.

A statistical design of experiments has become a must in all modern investigations The design of experiments facilitates a systematic and controlled procedure for understanding sensitivity of the variables and the reliability of various inferences.

For the present study 2^{7-4} fractional factorial design(34) was used. The range of variables was divided in three sets, each set consists of 16 experiments. The lower and upper limits of the variables are represented by '+' and '-' signs. Table 4.6 gives the upper and lower limits, for three sets of theseven variables. Enrichments of uranium for the three different sets (E_1, E_2, and E_3) are tabulated in Table 4.7. The average effects of all variables for the three sets are tabulated in Table 5.1 and a sample calculation is given in the Appendix B.

Table 5.1

Set.No.	X_1E	X_2E	X_3E	X_4E	X_5E	X_6E	X_7E
1.	-0.210	-0.130	-0.658	0.960	0.175	-0.050	-0.446
2.	-9.148	-2.254	-7 143	83.712	9.550	-0.829	-4.128
3.	-10.097	-12.406	-4.860	70.223	-4.584	-11.923	-20.560

TABLE 4.6

Set. No.	Weight of Uranium (mg) x_1		Weight of Molybdenum (mg) x_2		Weight of Benzethonium Chloride (Mg) x_3		Normality of hydrochloric acid x_4		Reflux ratio (ml/min) x_5		Feed Point (cm) x_6		Gasflow Rate (ml/min) x_7	
	Lower	Higher	Lower	Higher	Lower	Higher	Lower	Higher	Lower	Higher	Lower	Higher	Lower	Higher
1.	1.0	3.0	1.0	2.0	150.0	200.0	1.0	4.0	0.0	1.0	0.0	6.0	10.0	15.0
2.	3.0	5.0	2.0	3.0	200.0	250.0	4.0	8.0	1.0	2.0	6.0	12.0	15.0	20.0
3.	5.0	7.0	3.0	3.5	250.0	300.0	8.0	12.0	2.0	2.5	12.0	18.0	20.0	25.0

TABLE 4.7

FRACTIONAL FACTORIAL DESIGN OF EXPERIMENTS

No.	X_1	X_2	X_3	X_4	X_5	X_6	X_7	E_1	E_2	E_3
1.	-1	-1	-1	+1	+1	+1	-1	2.820	81.5	1.148
2.	+1	-1	-1	-1	-1	+1	+1	2.428	2.978	49.5
3.	-1	+1	-1	-1	+1	-1	+1	2.342	2.450	69.0
4.	+1	+1	-1	+1	-1	-1	-1	2.305	85.2	1.068
5.	-1	-1	+1	+1	-1	-1	+1	4.36	70.0	0.624
6.	+1	-1	+1	-1	+1	-1	-1	2.105	5.28	95.5
7.	-1	+1	+1	-1	-1	+1	-1	2.105	2.733	85.4
8.	+1	+1	+1	+1	+1	+1	+1	4.31	110.0	0.614
9.	+1	+1	+1	-1	-1	-1	+1	2.17	3.037	81.1
10.	-1	+1	+1	+1	+1	-1	-1	3.07	101.0	0.763
11.	+1	-1	+1	+1	-1	+1	-1	2.90	93.5	0.968
12.	-1	-1	+1	-1	+1	+1	+1	2.10	2.375	2.998
13.	+1	+1	-1	-1	+1	+1	-1	1.25	2.95	98.4
14.	-1	+1	-1	+1	-1	+1	+1	2.375	60.0	0.685
15.	+1	-1	-1	+1	+1	-1	+1	2.20	92.0	0.645
16.	-1	-1	-1	-1	-1	-1	-1	2.165	2.70	86.4

The following conclusions can be drawn from the above results

1. An increase in the concentration of uranium and molybdenum decreases the enrichment of uranium. The following concentrations of uranium and molybdenum are recommended.

1.0 mg of uranium

1.00 mg of molybdenum

The aoove conclusions is based on the range concentrations used in the present study.

2. Enrichment of uranium increases with the value of the benzethonium chloride concentration upto 250 mg and then decreases. The following value is recommended:

Concentration of benzethonium chloride = 250 mg/100 ml

3. Enrichment of uranium increases upto 8N hydrochloric acid and decreases with the further increase in normality of the acid.

Recommended value of normality of hydrochloric acid is 8N.

4. Enrichment of uranium increases with the reflux - ratio upto 2 ml per minute and then decreases with further increase in the reflux rate. The recommended value of reflux rate is 2 ml/min.

5. Enrichment of uranium decreases with an higher feed point location. Therecommended location is datum level that is just at the surface of the liquid pool.

6. Enrichment increases with an increase in gas velocity in the range of 10-15 ml/min and enrichment decreases on increase in gas velocity. Recommended value is 15 ml per minute.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Uranium can be fractionated from molybdenum by the foam fractionation technique when both the ions are present in aqueous solution at dilute concentration. Benzethonium chloride as a surface active agent for the foam fractionation is quite satisfactory. Enrichment of uranium is the highest when benzethonium chloride concentration is 250 mg/100 ml of solution a value which is slightly less than its critical micelle concentration. Best enrichment of uranium can be obtained when 8N hydrochloric acid solutions are used. A gas flow rate of 15 ml/min is recommended. Recommended reflux rate is 2 ml/min and the feed point location is just at the level of liquid pool. Higher uranium enrichment are possible at a concentration of 1 mg per 100 ml of solution.

Recommendations

Initial volume of the solution could be a factor for further study. Some work is necessary to identify ionic specy of uranium that is becoming surface active at 8N hydrochloric acid solution. A semi pilot plant is recommended. The study can be extended to the fractionation of multicomponent system. Suitable mathematical modelling for the system should be attempted.

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APPENDIX A

ANALYSIS OF URANIUM AND MOLYBDENUM

1. COLORIMETRIC DETERMINATION OF URANIUM (32).

REAGENTS:

1. Ammonium Thiocynate: 500 gms of ammonium thiocynate (ana-lar grade) per litre of aqueous solution.

2. Stannous chloride. 50 gms of stannous chloride dihydrate dissolved in 50 ml of concentrated hydrochloric acid, diluted to 500 ml with water and then filtered to give a clear solution.

3. Hydrochloric acid 5N hydrochloric acid solution was used.

4. Potassium hydroxide: 1N solution

Procedure:

A blank solution containing 4 mg of molybdenum in 2 ml of 5N hydrochloric acid reagent was diluted to 45 ml and titrated to a pH of 1.0 with 1N potassium hydroxide. It was then diluted to 50 ml by the addition of about 2.8 ml of distilled water.

A series of solutions containing different quantities of uranium varying from 1 mg to 9 mg and 2 mg of molybdenum were prepared in 1 ml of 5N hydrochloric acid. 1.1 ml of potassium hydroxide (i.e. half the quantity of it required for the blank solution) was added in each of the solutions and then diluted to 25 ml with water. 10 ml of the blank and of each of the above uranium solutions were transferred into 25 ml measuring flasks.

2 ml of the stannous chloride reagent and 7 ml of thiocynate reagent were added to each of the above solutions and then they were diluted to 25 ml with distilled water. All of these solutions were centrifuged to remove suspension. Spectronic-20 was adjusted to give 100% transmittance with blank solution. Then transmittance for other solutions were measured. The % transmittance was plotted against the weight of uranium present per 25 ml solution to give the calibration curve. The work is presented in Fig.A.1.A light filter of 365 mμ wave length was used throughout the experiments.

In order to determine the quantity of uranium in an unknown solution, 10 ml of sample was taken and pH was adjusted to 1.0 with potassium hydroxide, then 2 ml of stannous chloride reagent and 7 ml of thiocynate reagent were added, and the solution was diluted to 25 ml. Solution was then centrifuged to give a clear solution. The spectronic 20 was then adjusted to give 100% transmittance with a blank solution prepared simultaneously. The transmittance of unknown solution was then me measured and the amount of uranium was then determined from the calibration curve.

DETERMINATION OF MOLYBDENUM (33)

REAGENTS USED.

1. Dithiol solution: 0.15 g of dithiol was added to 100 ml of 0.25N sodium hydroxide and then solution was kept in a refrigerator.

2. Butyl acetate

3. 10N sulfuric acid

4. 85% phosphoric acid

5. Citric acid

Procedure:

A series of solutions containing different quantities of molybdenum varying from 0 to 4 mg in 4 ml of 10N sulfuric acid were prepared. 3 drops of 85 percent phosphoric acid and 0.5 g of citric acid were then added to each of the samples which were then diluted with water to 20 ml. 2 ml. of dithiol solution was then added. These solutions were then kept at room temperature for 2 hours. After adding 10 ml. of butyl acetate, the solutions were shaken for 5 minutes. Water layer was then removed and the solutions were made to 25 ml with butyl acetate. All of these solutions were then centrifuged to remove suspended material. Then transmittance for the solutions was measured using spectronic-20. The percentage transmittance was plotted (on the logarithmic scale) against the weight of molybednum (on the ordinary scale) to obtain the calibration curve. A 565 mμ wave length filter was used.

The amount of molybdenum in solutions of unknown concentrations was then determined from calibration curve.

TABLE A-1

CALIBRATION CURVE FOR URANIUM

Sl. No.	Weight of Uranium (mg)	% Transmittance
1.	0.0	100
2.	1.0	74
3.	2.4	52
4.	3.8	40
5.	5.0	27
6.	5.95	21
7.	7.3	15
8.	8.15	12
9.	9.0	9.6

TABLE A-2

CALIBRATION CURVE FOR MOLYBDENUM

Sl. No.	Weight of Molybdenum (mg.)	% Transmittance
1.	0	100
2.	1	49
3.	2	25
4.	3	14
5.	4	6.4

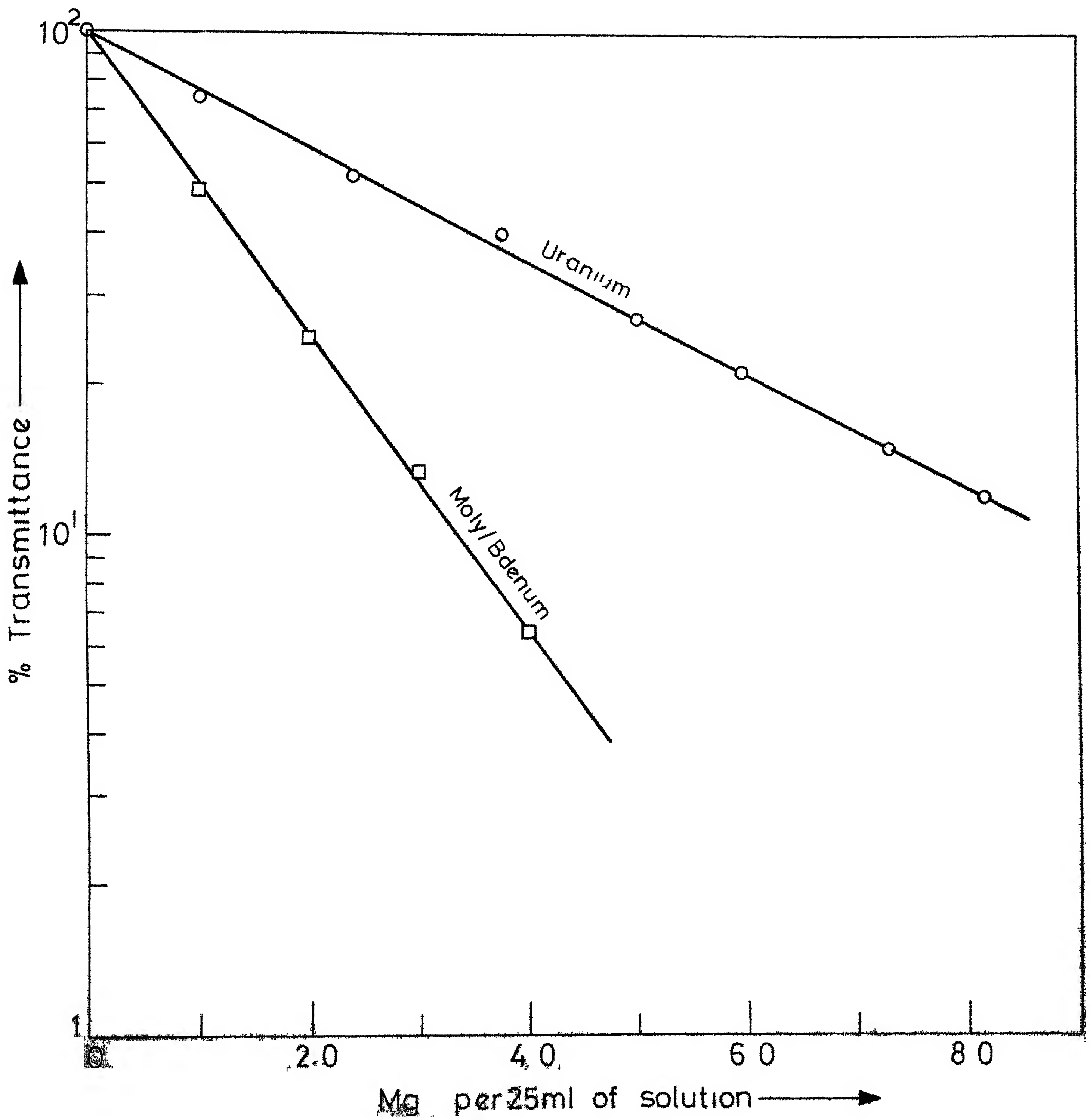

FIG (A-I) CALIBRATION CURVE

APPENDIX B

SAMPLE CALCULATIONS

1. Calculation of Enrichment of Uranium(E)

Calculation shown below is for 1N hydrochloric acid and 15 ml/min gas flow rate.

$$\text{Enrichment} = \frac{\text{Concentration of uranium infoamate}}{\text{Concentration of uranium inraffinate}}$$

Date: % transmittance of foamate = 79.2%

% transmittance of raffinate = 89.6%

From Fig. A-1,

Concentration of foamate = 0.85 mg U/25 ml

Concentration of raffinate = 0.38 mg U/25 ml

$$\text{Therefore, Enrichment} = \frac{0.85}{0.38} = 2.238$$

2. Calculation for Finding Average Effect of Variable:

Calculation done here is for finding average effect of uranium concentration in set 1.

$$\underline{X_1 E} = \frac{1}{8}(-2.820 + 2.428 - 2.342 + 2.305 - 4.36 + 2.105 - 2.105 + 4.31 + 2.17 - 3.07 + 2.90 - 2.10 + 1.25 - 2.375 + 2.20 - 2.165)$$

$$= -0.21$$